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STUDIES ON THERMAL STABILITY OF MIXED METAPHOSPHATES $KLa(PO_3)_4$ AND $K_2La(PO_3)_5$

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Within an investigation of the phase equilibria in the binary system $La(PO_3)_3$-KPO_3, the thermal behaviour of the mixed metaphosphates $KLa(PO_3)_4$ and $K_2La(PO_3)_5$ has been examined.

There has recently been considerable interest in the lanthanides and their compounds (e.g. phosphates). A number of publications have described methods of obtaining mixed alkali metal-rare earth metaphosphates and also their X-ray structural and spectrophotometric examinations [1-3]. There is likewise and increasing number of literature reports on the phase equilibria in the binary systems M^IPO_3-$Ln(PO_3)_3$ (where M^I = alkali metal, and Ln = rare earth). It can be concluded from these that the initial metaphosphates may form the following types of compounds: $M^ILn(PO_3)_4$ and $M^I_2Ln(PO_3)_5$ [4-8].

At present, phase examinations on the ternary system La_2O_3-K_2O-P_2O_5 are being carried out in this laboratory. There is a known binary section KPO_3-$La(PO_3)_3$ in this system [8], and the existence of potassium-lanthanum metaphosphates, $KLa(PO_3)_4$ and $K_2La(PO_3)_5$, has been discovered. Both compounds are formed incongruently, at 880 and 770°, respectively.

Experimental

The following commercial reagents were used for the investigations: KH_2PO_4 analytical grade, La_2O_3 99.9 %, $NH_4H_2PO_4$ analytical grade, $La(NO_3)_3$ analytical grade, and H_3PO_4 85 % analytical grade. KPO_3, $La(PO_3)_3$, LaP_5O_{14}, $LaPO_4$, $KLa(PO_3)_4$ and $K_2La(PO_3)_5$ were synthesized in this laboratory. $La(PO_3)_3$ was produced from La_2O_3 and H_3PO_4 by

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sintering a stoichiometric mixture of these substances at 800° for 3 days. LaP_5O_{14} was prepared by sintering La_2O_3 and H_3PO_4 (in the molar ratio P/La = 20) at 600° for 1 day and at 700° for 2 days. $LaPO_4$ was obtained by crystallization from an aqueous solution of 0.4 % La_2O_3 (as $La(NO_3)_3$) and 15 % P_2O_5 (as H_3PO_4). The mixture was placed in a round-bottomed flask and was brought to the boil under a reflux condenser and held there for 6 h. The phosphate $KLa(PO_3)_4$ was prepared by sintering 1:1 stoichiometric mixture of KPO_3 and $La(PO_3)_3$ at 800° for 3 days. The phosphate $K_2La(PO_3)_5$ was produced by sintering a 1:2 molar mixture of $La(PO_3)_3$ and KPO_3 at 700° for 3 days.

The investigations were carried out by differential thermal analysis, powder X-ray diffraction and IR spectroscopy. The thermal analysis was performed by means of a derivatograph type 3427 (MOM, Hungary) within the temperature range 20-1300°, at a heating rate of 10 deg/min, in a platinum cup, in air atmosphere. The reference substance was Al_2O_3. The powder X-ray analysis was performed in an HZG-4 diffractometer with CuK_α radiation.

Results

The thermal and X-ray investigations showed that the mixed metaphosphates $KLa(PO_3)_4$ and $K_2La(PO_3)_5$ are stable in the temperature range up to 840 and 770°, respectively, in the section KPO_3-$La(PO_3)_3$. This is confirmed by the DTA curves presented in Fig. 1.

In the ternary system La_2O_3-K_2O-P_2O_5, in the part rich in P_2O_5, it was found that the temperature range of stability of the mixed metaphosphates under discussion undergoes changes.

The behaviour of $KLa(PO_3)_4$ was examined in the presence of various quantities of $NH_4H_2PO_4$ (as a source of P_2O_5), LaP_5O_{145} and $LaPO_4$. Samples of $KLa(PO_3)_4$ containing 5 and 15 wt% of P_2O_5 were sintered at 600° for 4 h, and then at 800° for 1 h. X-ray analysis of the sinters showed that: (a) the addition of 5% P_2O_5 caused some decomposition of $KLa(PO_3)_4$ to $La(PO_3)_3$ at 800° only, (b) the addition of 15% P_2O_5 caused the partial decomposition of $KLa(PO_3)_4$ to LaP_5O_{14} at 600°, and at 800° there was complete decomposition to $La(PO_3)_3$. X-ray examinations revealed the presence of $KLa(PO_3)_4$ and LaP_5O_{14} in different mixtures of $KLa(PO_3)_4$ and LaP_5O_{14} sintered at 700° for 4 h. The same preparations sintered at 800° for 2 h were a mixture of $La(PO_3)_3$ and LaP_5O_{14}. Figure 2a presents a DTA curve of a mixture with the composition 80 wt% of $KLa(PO_3)_4$ and

20 wt% of LaP_5O_{14} . The effect at 750° in the curve results from the decomposition of $KLa(PO_3)_4$.

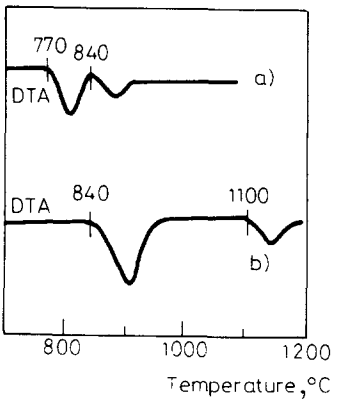

Fig. 1 DTA curves of a) $K_2La(PO_3)_5$, b) $KLa(PO_3)_4$

Thermal analysis of preliminarily synthesized preparations forming a mixture of $KLa(PO_3)_4$ and $LaPO_4$ with different compositions showed that an endothermic effect appeared systematically in the temperature range 800-840°. X-ray analysis of these mixtures sintered at 760° for 20 h demonstrated the presence of $KLa(PO_3)_4$ and $LaPO_4$, while thermal

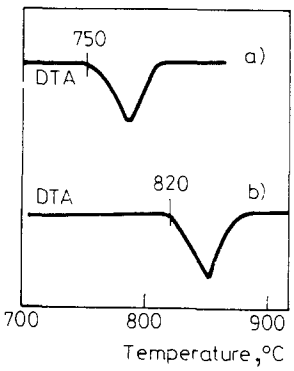

Fig. 2 DTA curves of samples containing: a) 80 wt% $KLa(PO_3)_4$, 20 wt% LaP_5O_{14}, b) 90 wt% $KLa(PO_3)_4$, 10 wt% $LaPO_4$

analysis after heating showed the presence of $La(PO_3)_3$ and $LaPO_4$. Hence, the addition of $LaPO_4$ does not really influence the range of $KLa(PO_3)_4$ stability.

The behaviour of the mixed metaphosphate $K_2La(PO_3)_5$ in the presence of various quantities of P_2O_5 (in the form of $NH_4H_2PO_4$) was also examined. Samples of $K_2La(PO_3)_5$ containing 5 or 20 wt% of P_2O_5 were sintered at 300° for 4 h and at 500° for 4 h again. X-ray analysis of the sinters obtained in this way showed that even at 500°: a) $K_2La(PO_3)_5$ undergoes partial decomposition to $KLa(PO_3)_4$ in the presence of 5% P_2O_5, b) complete decomposition to $KLa(PO_3)_4$ occurs in the presence of 20% P_2O_5.

To summarize, it should be pointed out that $KLa(PO_3)_4$ is a more stable compound than $K_2La(PO_3)_5$. The temperature of $KLa(PO_3)_4$ decomposition and the nature of the products formed depend on the additives and their proportions.

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Zusammenfassung — Innerhalb einer Studie über Phasengleichgewichte im binären System $La(PO_3)_3$ - KPO_3 wurde das Verhalten der Mischsalze $KLa(PO_3)_4$ und $K_2La(PO_3)_5$ in Hinsicht auf eine thermische Behandlung untersucht.